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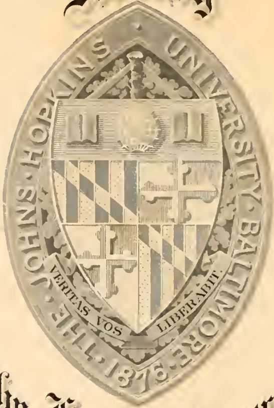

of the Johns Hopkins University

A FURTHER INVESTIGATION
OF THE
CHLORIDES OF ORTHOSULPHOBENZOIC ACID
AND PARANITROORTHOSULPHOBENZOIC ACID.

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A Dissertation Presented to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy

by

Willis B. Holmes.

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Baltimore, Maryland,
June, 1899.

n. 340

Acknowledgement.

This work was undertaken at the suggestion of Professor Ira Remsen and carried on under his personal direction. The author takes this opportunity of expressing to him his sincere gratitude for the interest which he has taken in the work and for the instruction received in the laboratory and lecture room. He also wishes to express his obligations to Professors Morse, Clark, Dr. Matthews and Dr. Shattuck.

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Introduction.

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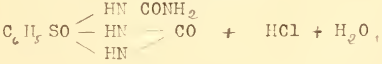
In 1880 Elander (1) tried the action of urea upon benzenesulphone chloride. He heated the chloride and urea in the proportion of one molecule of the former to three molecules of the latter at 100° and obtained a well crystallized body of the following composition.

$C_6H_5\ SN_4H_5C_2O_3$.

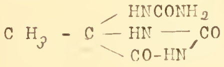
Two molecules of urea entered into the reaction with the elimination of water and hydrochloric acid. He considered that one molecule of urea reacted with the chlorine atom splitting off hydrochloric acid, while a second molecule of urea attacked the oxygen of the sulphone group with the elimination of water. He expressed the structure of this compound as follows;

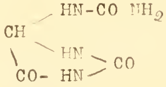
$C_6H_5SO_2Cl + 2\ H_2N\ CO\ NH_2 =$



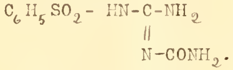
$$C_6H_5SO\left\langle\begin{matrix}HN\ CONH_2\\ HN\\ HN\end{matrix}\right\rangle CO + HCl + H_2O,$$

considering it an analogue of pyruvile and allantoin



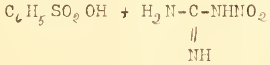


As the oxygen of the sulphone group is removed only with great difficulty, it seemed very improbable that the above reaction should take place. This work was recently repeated in this laboratory and entirely different results obtained. The same method of proceedure was followed and the same substance isolated. This compound on boiling with fuming nitric acid broke down into benzenesulphonic acid and nitroguanidine. On hydrolysis with dilute hydrochloric acid or barium hydroxide, ammonia and carbon dioxide ~~was~~ were given off, and the final product obtained was the guanidine salt of benzene sulphonic acid. These two reactions can only be explained by the following structure



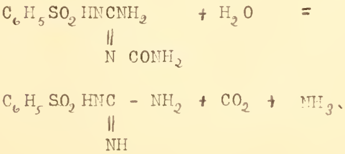
$$C_6H_5SO_2-HN-\underset{\substack{\| \\ N-CONH_2.}}{C}-NH_2$$

With fuming nitric acid this gives



$$C_6H_5SO_2OH + H_2N-\underset{\substack{\| \\ NH}}{C}-NHNO_2$$

and by hydrolysis



$$C_6H_5SO_2HN\underset{\substack{\| \\ N\ CONH_2}}{C}NH_2 + H_2O = C_6H_5SO_2HN\underset{\substack{\| \\ NH}}{C}-NH_2 + CO_2 + NH_3.$$

One molecule of urea enters into reaction with the chloride, and the second urea molecule attacks the oxygen of the urea residue with the elimination of water.

In view of these interesting results the action of urea upon the chlorides of orthosulphobenzoic acid was tried, and the results obtained are given below.

PREPARATION OF MATERIALS.

Chlorides of Orthosulphobenzoic Acid.

As the method of preparing these chlorides has been subject to numerous changes it seems best to give a brief account of it here. The saccharin~~e~~ now obtain~~ed~~able on the market is very nearly pure. Two hundred grams are placed in a large evaporating dish with three liters of water and 250c.c. of hydrochloric acid. This mixture is then boiled for five or six hours, keeping the volume constant, until the sweet taste of saccharin~~e~~ has entirely disappeared. It is then evaporated to about one liter, allowed to cool, filtered and evaporated to dryness. The acid ammonium salt of orthosulphobenzoic acid thus obtained is washed with alcohol until perfectly white. It is then dissolved in enough water so that the hot solution is about half saturated, allowed to cool and a little more than the required amount,

two molecules of potassium hydroxide added. When cold the addition of hydrochloric acid precipitates the acid potassium salt of orthosulphobenzoic acid in white plates. From the filtrate on evaporation more of the acid potassium salt can be obtained.

Fifty grams of the dried acid potassium salt are placed in a large mortar with 2 1/2 molecules of phosphorus pentachloride and the mixture intimately ground until reaction ensues. The resulting oil is then transferred to an evaporating dish, and placed on a steam-bath for several hours, until most of the phosphorus oxychloride has distilled off. It is then poured into a large bottle containing ice-water and shaken vigorously. After shaking with several changes of water, it is ready for further use.

To obtain a mixture of the dry chloride the oil is placed in a mortar with cracked ice and ground until it becomes solid. It is then filtered, washed with ice-water and pressed between drying-paper, care being taken not to touch the product or have anything warm near it as the mixture melts at 21°. It is then dried in a desiccator in a cool place. One hundred grams of the mixed chlorides contain about sixty grams of the unsymmetrical chloride.

To obtain the symmetrical chloride the oil is at

once dissolved in ether and transferred to a large separating-funnel containing ice and water. Ammonia is then added till after shaking for a few minutes the presence of ammonia is still detected. Hydrochloric acid is then added to neutralize the free ammonia, the ethereal solution washed, separated and dehydrated with calcium chloride. On evaporating off the ether the chloride is obtained. This can be obtained perfectly pure by crystallizing from pure ligroin (b.pt. 90° - 125°).

The product melting at 21° formerly considered to be the unsymmetrical chloride has been shown to be a mixture of the two chlorides.(1) The pure unsymmetrical chloride melts at 40° and is prepared as follows: The neutral potassium salt of orthosulphobenzoic acid obtained by neutralizing the acid potassium salt with potassium hydroxide is heated in a sealed tube for four hours with 1 1/2 molecules of phosphorus oxychloride at 135°. The product is transferred to a mortar ground up with several changes of ice-water, filtered, dried and crystallized from pure ligroin. The yield is about fifty per cent.

A mixture of these chlorides has the property of crystallizing apparently as a chemical individual. It

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(1) B, 11, 1898, p.1653.

crystallizes in long radiating tufts which melt at 21° and is not changed by further crystallization.

Chlorides of Paranitroorthosulphobenzoic Acid.

The symmetrical chloride of paranitroorthosulphobenzoic acid was prepared as described by Remsen and Henderson.(1)

In the preparation of the unsymmetrical chloride the ~~results~~ method of Remsen and Hollis(2) ~~were~~ was not followed. A much better method of preparation was as follows: The neutral potassium salt of paranitroorthosulphobenzoic acid is heated with 1 1/2 molecules of phosphorus oxychloride in a sealed tube for four hours at 135°. The product is then transferred to a mortar ground up with several changes of ice water, filtered, dried and recrystallized from pure ligroin. Only the unsymmetrical chloride was obtained and was identical with that described by Hollis. The reaction is a very clean one with a uniform yield of fifty per cent.

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(1) Inaug. Diss. J.H.U., 1897.
(2) Inaug. Diss. J.H.U., 1896.

ACTION OF UREA ON THE CHLORIDES OF ORTHO-SULPHOBENZOIC ACID.

Symmetrical Chloride.

A mixture of the symmetrical chloride with urea in the proportion of one molecule of the former to four of the latter was heated in a test-tube at various temperatures. When heated over a free flame or above the melting-point of urea violent reaction took place with a considerable evolution of heat. Hydrochloric acid was given off and a considerable quantity of biuret was formed. As the heat of the reaction was sufficient to destroy any urea residue no attempt was made to isolate the products.

When the mixture was heated at 100° , the reaction proceeded very slowly and quietly without the evolution of heat. A mixture of the chloride and urea in the proportion of one molecule to four was heated for several days at 100 in a test-tube. At first, the mixture became liquid, forming two distinct layers. Stirring greatly facilitated the reaction. In the course of a few hours the mixture became pasty, and stirring was necessary in order to insure a thorough mingling of the two constituents. At the end of two days the mass became hard. A little hydrochloric acid was

given off during the experiment.

The hard cake formed was then dissolved in hot water On cooling there separated out a small quantity of a substance soluble in hot but sparingly soluble in cold water. This body contained no sulphur and appeared to be biuret. The mother-liquor on concentration yielded a very beautiful crystalline substance and small quantities of ammonium chloride. This substance had a strong crystallizing power and usually appeared in long colorless monoclinic prisms. It melted at 266°, was moderately soluble in water, but insoluble in alcohol or ether. It acted like an ammonium salt, giving off ammonia in the cold with weak alkalies. The yield was about fifty-five per cent of the theoretical and no other product was obtained.

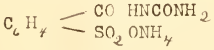
Unsymmetrical Chloride.

The same method of procedure was followed with the unsymmetrical chloride. The chloride with urea in the proportion of one molecule to four was heated in a test-tube at 100° for several days. Reaction took place much more quickly than with the symmetrical chloride. The resulting product was dissolved in hot water. On cooling there separated out a small quantity of a substance soluble in hot

but sparingly soluble in cold water. This body contained no sulphur and was identical with that obtained from the symmetrical chloride. From the mother-liquor on evaporation there crystallized out the same characteristic monoclinic prisms as were obtained from the symmetrical chloride and a small quantity of ammonium chloride. This substance melted at 266° was moderately soluble in water, insoluble in alcohol or ether. It gave off ammonia in the cold with weak alkalies, and was identical with the product obtained from the symmetrical chloride. The yield was about fifty-five per cent of the theoretical. On analysis, it gave the following composition $C_6H_4SO_5C_2H_7N_3$:

	Theory	Found	
C	36.75	36.61	36.70
H	4.22	4.29	4.28
S	12.27	12.31	12.38
N	16.14	16.34	16.10

It proved to be the ammonium salt of benzoylureaorthosulphonic acid.



$$C_6H_4 \begin{cases} CO\,HNCONH_2 \\ SO_2\,ONH_4 \end{cases}$$

Action of Hydrochloric Acid.

On boiling with dilute hydrochloric acid the ammonium salt was hydrolyzed to the acid ammonium salt of orthosulphobenzoic acid. This on treatment with potassium hydroxide gave off ammonia and on acidifying with hydrochloric acid gave the characteristic acid potassium salt of orthosulphobenzoic acid.

Action of Potassium Hydroxide.

The ammonium salt was boiled with a dilute solution of potassium hydroxide for six hours. Ammonia was constantly given off, showing a slow hydrolysis. On evaporating the solution there separated out the potassium salt of orthobenzaminesulphonic acid. This salt was very soluble in water and crystallized in monoclinic plates. It contained one molecule of water of crystallization and was identical with the potassium salt of orthobenzaminesulphonic acid described by Remsen and Karslake.(1) This showed that the urea residue was in the carbonyl group.

0.1339g. gave .0096g. H_2O

0.1546g. gave .0111g. H_2O

0.2099g. gave .0769G. K_2SO_4

0.1386g. gave .0505g. K_2SO_4

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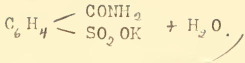
(1) Am. Chem. Jour. 18, 826.

Calculated for 
$C_6H_4<{}^{CONH_2}_{SO_2OK} + H_2O.$

	~~Theory~~	Found	
H_2O	7.04	7.17	7.18
K	16.32	16.43	16.39

Action of Barium Hydroxide

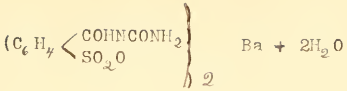
A solution of the ammonium salt was treated in the cold with an excess of barium hydroxide. Ammonium was given off and, after allowing the solution to stand for some time, the excess of barium hydroxide was removed by carbon dioxide. From the filtered solution on evaporation ~~there~~ separated out crystals of the barium salt of benzoylureaorthosulphonic acid. This salt was sparingly soluble in water and separated out in clusters of transparent diamond-shaped crystals. It crystallized with two molecules of water of crystallization and effloresced on exposure to the air becoming opaque.

0.3346g. gave .0181g. H_2O

0.2109g. gave..0110g. H_2O

0.1998g. gave .0742g. Ba SO_4

0.1972g. gave .0732g. $BaSO_4$

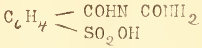
Calculated for 

$$\left(C_6H_4<\begin{matrix}COHNCONH_2\\SO_2O\end{matrix}\right)_2 Ba + 2H_2O$$

Theory		Found	
$2H_2O$	5.47	5.40	5.22
Ba	21.98	21.82	21.80

Benzoylureaorthosulphonic Acid.

This acid was made by treating the barium salt with an equivalent amount of sulphuric acid. It ~~was~~ is a strong acid extremely soluble in water, separating out as a silky mass only when the solution was evaporated to a thick syrup. No attempt was made to analyze it and from a study of its salts its ~~constitution~~ composition proved to be

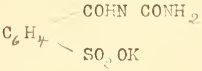


$$C_6H_4<\begin{matrix}COHN\ CONH_2\\SO_2OH\end{matrix}$$

Potassium Salt.

This salt was made by neutralizing the free acid with potassium hydroxide. It was moderately soluble in water, and separated out in especially well-defined, colorless, monoclinic prisms. It contained no water of crystallization and melted at 286°.

0.2406 g. gave 0.0740 g. K_2SO_4
0.2465 g. gave 0.0753 g. K_2SO_4

Calculated for 
$C_6H_4\begin{matrix}\diagup COHN\ CONH_2\\ \diagdown SO_2OK\end{matrix}$

	Theory	Found	
K	13.85	13.80	13.71

Sodium Salt -

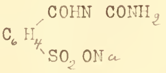
This salt was made by neutralizing the free acid with sodium hydroxide. It separated out in thick, opaque, poorly defined prisms, apparently of orthorhombic habit. It was quite soluble in water, contained one molecule of water of crystallization, and effloresced on exposure to the air.

0.6932 g. gave .0430 g. H_2O

.5936 g. gave .0369 g. H_2O

.1826 g. gave .0486 g. Na_2SO_4

.2274 g. gave .0606 g. Na_2SO_4

Calculated for 
$C_6H_4\begin{matrix}\diagup COHN\ CONH_2\\ \diagdown SO_2ONa\end{matrix}$ + H_2O

	Theory	Found	
H_2O	6.33	6.20	6.22
Na	8.66	8.59	8.62

Lead Salt

This salt was made by neutralizing the free acid with lead carbonate. It was very soluble in water separating out in clusters of thin, transparent, tabular plates. The crystals were not well defined, contained three molecules of water of crystallization, and effloresced on exposure to the air, becoming opaque.

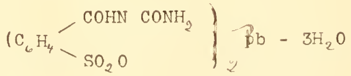
0.5148 g. gave .0371 g. H_2O

.3417 g. gave .0254 g. H_2O

.1693 g. gave .0746 g. Pb SO_4

.1742 g. gave .0770 g. Pb. SO_4

Calculated for



$$\left(C_6H_4\begin{matrix} \diagup COHN\ CONH_2 \\ \diagdown SO_2O \end{matrix}\right)_2 Pb - 3H_2O$$

Theory		Found	
$3H_2O$	7.24	7.20	7.43
Pb	29.85	30.00	30.05

Copper Salt

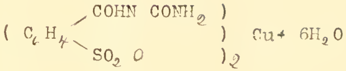
This salt was made by dissolving freshly prepared copper oxide in the free acid. It was moderately soluble in water, crystallized in clusters of long blue prisms and contained six molecules of water of crystallization.

.1957 g. gave .0324 g. H_2O

.2585 g. gave .0422 g. H_2O

.2010 g. gave .0292 g. CuO

.2161 g. gave .0315 g. CuO

Calculated for 

$$\left(C_6H_4 \begin{matrix} \diagup COHN\ CONH_2 \\ \diagdown SO_2\ O \end{matrix} \right)_2 Cu + 6H_2O$$

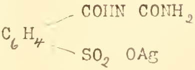
Theory		Found	
$6H_2O$	16.45	16.60	16.33
Cu	11.52	11.59	11.62

Silver Salt

This salt was prepared by dissolving silver oxide in a solution of the free acid. It ~~was~~ is moderately soluble in water, crystallizes in clusters of thick-pointed poorly defined prisms, contains no water of crystallization and darkens on exposure to the light.

.2188 g. gave .0675 g. Ag.

.2130 g. gave .0658 g. Ag.

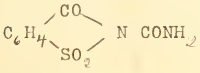
Calculated for 

$$C_6H_4 \begin{matrix} \diagup COHN\ CONH_2 \\ \diagdown SO_2\ OAg \end{matrix}$$

Theory		Found	
Ag	30.74	30.85	30.90

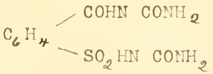
Several explanations ~~for~~ of the formation of the ammonium salt of benzoylureaorthosulphonic acid are possible. It is a secondary product formed after the heated mass had been dissolved in water. The hydrochloric acid in the aqueous solution decomposed the original compound with the formation of ammonium chloride. All attempts to isolate the original product failed. The mass of chloride and urea after heating was extracted with ether and chloroform,but nothing was obtained. This probably disproves the theory that the chlorine atom of the carbonyl group was acted upon and the chlorine of the sulphonyl group removed by subsequent hydrolysis. It completely dissolved in alcohol,showing that the ammonium salt was not the original compound. On account of its extreme solubility in alcohol or water and from its poor crystallizing power,it was impossible to separate it from the large amount of urea present.

There are two possible theories to account for the formation of the ammonium salt. One molecule of urea may have reacted with one molecule of the chloride to form a ureid compound.



which on hydrolysis would take up a molecule of water and give the free sulphonic acid. This with the ammonium chlo-

ride formed from the decomposition of the urea by hydrochloride would give the ammonium salt. On the other hand, two molecules of urea may have reacted with one molecule of the chloride to form a diureid.



$$C_6H_4\begin{cases}COHN\ CONH_2\\SO_2HN\ CONH_2\end{cases}$$

The urea residue in the sulphonyl group was then hydrolyzed to the ammonium salt. This latter view seems the mo~~st~~re probable.

ACTION OF UREA ON THE CHLORIDES OF PARANITRO-ORTHOSULPHOBENZOIC ACID.

Symmetrical Chloride

As a rule the derivatives formed from the chlorides of paranitroorthosulphobenzoic acid are less soluble than the corresponding derivatives formed from the chlorides of orthosulphobenzoic acid. In view of this fact, the action of urea upon these chlorides was tried, to see if some of the intermediate products of the reaction could not be isolated.

A mixture of the chloride and urea in the proportion

of one molecule to four was heated at different temperatures. When heated over a free flame or above the melting-point of urea violent reaction took place. Hydrochloric acid was given off and there was a considerable evolution of heat. As the heat of the reaction was sufficient to destroy any urea residue no attempt was made to isolate the products.

At 100° the reaction proceeded very slowly and quietly without the evolution of heat. A mixture of the chloride and urea in the proportion of one molecule to four was heated for two days at 100°. At first the mass became liquid, forming two distinct layers. As the reaction proceeded stirring was necessary in order to insure a thorough mingling of the two constituents. Reaction took place more slowly than with the symmetrical chloride of orthosulphobenzoic acid.

The hard cake formed was dissolved in hot water. On cooling, there separated out a small quantity of a substance soluble in hot, but sparingly soluble in cold, water. It contained no sulphur and appeared to be biuret. The mother-liquor on concentration yielded small quantities of ammonium chloride and a well crystallized substance of a pale lemon color. This body crystallized in diamond-shaped

plates and melted at 273°. It was moderately soluble in water, insoluble in alcohol or ether. It acted like an ammonium salt giving off ammonia in the cold with weak alkalies. The yield was about 55% and no other product was obtained.

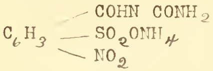
Unsymmetrical Chloride.

The same method of procedure was followed with the unsymmetrical chloride. Reaction took place much more quickly than with the symmetrical chloride. The resulting product was dissolved in hot water. On cooling there separated out a small quantity of a substance soluble in hot, but sparingly soluble in cold, water. This body was identical with that obtained from the symmetrical chloride and was probably biuret. From the mother-liquor there separated out on evaporation the same diamond-shaped plates as were obtained from the symmetrical chloride. These melted at 273°, were moderately soluble in water insoluble in alcohol or ether. This body gave off ammonia in the cold when treated with weak alkalies. It contained no water of crystallization and was identical with the product obtained from the symmetrical chloride. The yield was about 60%. On analysis it gave the following results:

$C_8H_{10}O_7SN_4$

	Theory	Found	
C	31.34	31.13	
H	3.27	3.36	3.31
S	10.47	10.32	10.39
N	18.36	18.38	18.50

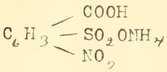
This substance proved to be the ammonium salt of paranitrobenzoylureaorthosulphonic acid.



$$\mathrm{C_6H_3}\begin{cases}\mathrm{COHN\ CONH_2}\\ \mathrm{SO_2ONH_4}\\ \mathrm{NO_2}\end{cases}$$

Action of fuming nitric acid.

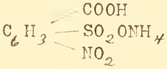
This salt was boiled with fuming nitric acid to see if any nitro-guanidine was formed as would be the case if one of the urea molecules had acted upon a urea residue. Nothing but the acid ammonium salt of paranitroorthosulphobenzoic acid was formed. This salt crystallized in hexagonal-shaped, monoclinic plates, and was very soluble in water. On treating a solution of this salt with potassium hydroxide, ammonia was given off and, on acidifying, ~~there~~ separated out the characteristic acid potassium salt of paranitroorthosulphobenzoic acid.

Calculated for 
$C_6H_3 \begin{cases} COOH \\ SO_2ONH_4 \\ NO_2 \end{cases}$

Theory		Found	
NH_3	6.43	6.39	6.38

Action of Hydrochloric Acid.

On boiling with dilute hydrochloric acid the ammonium salt was hydrolyzed to the acid ammonium salt of paranitroorthosulphobenzoic acid. It was identical with the salt obtained by the action of fuming nitric acid.

Calculated for 
$C_6H_3 \begin{cases} COOH \\ SO_2ONH_4 \\ NO_2 \end{cases}$

Theory		Found	
NH_3	6.43	6.51	6.41

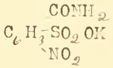
Action of Potassium Hydroxide.

The ammonium salt was boiled with an excess of a dilute solution of potassium hydroxide for six hours. Ammonia was given off during the entire time showing a slow hydrolysis. On concentrating the solution there separated out the potassium salt of paranitroorthobenzaminesulphonic acid. This salt ~~was~~ is very soluble in water, and separated out in thin yellowish plates. It contained no water of crystallization.

.1983 g. gave .0604 g. K_2SO_4

.2174 g. gave .0660 g. K_2SO_4

Calculated for



$C_6H_3\begin{cases}CONH_2\\SO_2OK\\NO_2\end{cases}$

	Theory	Found	
K	13.73	13.66	13.61

Action of Barium Hydroxide.

A solution of the ammonium salt was treated in the cold with an excess of barium hydroxide. Ammonia was given off and, after allowing the solution to stand for some time, the excess of barium was removed by carbon dioxide. From the filtered solution on evaporation there separated out crystals of the barium salt of paranitrobenzoylureaorthosulphonic acid. This salt crystallized in small yellow prisms and was sparingly soluble in water. It contained two molecules of water of crystallization.

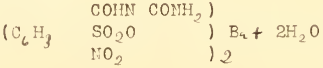
.3815 g. gave .0178 g. H_2O

.3864 g. gave .0182 g. H_2O

.2778 g. gave .0906 g. $BaSO_4$

.1678 g. gave .0546 g. $BaSO_4$

Calculated for



$\left(C_6H_3\begin{matrix}COHN\ CONH_2\\SO_2O\\NO_2\end{matrix}\right)_2 Ba + 2H_2O$

	Theory	Found	
$2H_2O$	4.81	4.66	4.71
Ba	19.20	19.15	19.08

Paranitrobenzoylureaorthosulphonic Acid.

This acid was made by treating the barium salt with the calculated amount of sulphuric acid. It ~~was~~ is a strong acid very soluble in water, separating out only when the solution ~~was~~ is evaporated nearly to dryness. No attempt was made to analyze it.

Potassium Salt.

This salt was made by neutralizing a solution of the free acid with potassium hydroxide . It has a marked crystallizing power, separating out in clusters of long, narrow prisms of a pale yellow color. It ~~was~~ is sparingly soluble in water and crystallizes with one molecule of water of crystallization.

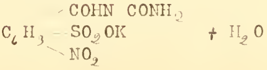
.3573 g. gave .0181 g. H_2O

.5992 g. gave .0312 g. H_2O

.3554 g. gave .0939 g. K_2SO_4

.2289 g. gave .0612 g. K_2SO_4

Calculated for



$$C_6H_3\begin{cases}COHN\ CONH_2\\ SO_2OK\\ NO_2\end{cases} + H_2O$$

Theory		Found	
H_2O	5.22	5.07	5.21
K	11.94	11.85	11.97

Sodium Salt.

The sodium salt was made by neutralizing a solution of the free acid with sodium hydroxide. It ~~was~~ is moderately soluble in water and of a pale yellow color. It ~~had~~ has two habits of crystallization. When a solution of the salt was cooled quickly it separated out in long silky needles containing four molecules of water of crystallization. These gave up water very quickly on exposure to the air. When the solution was cooled slowly the salt separated out in orthorhombic prisms containing one molecule of water of crystallization The needles on standing in the solution slowly changed to the orthorhombic prisms.

.2893 g. gave .0158 g. H_2O

.2262 g. gave .0126 g. H_2O

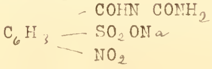
.3311 g. gave .0615 g. H_2O

.2637 g. gave .0484 g. H_2O

.2292 g. gave .0520 g. Na_2SO_4

.1878 g. gave .0432 g. Na_2SO_4

Calculated for



$$C_6H_3\begin{array}{l} - COHN\ CONH_2 \\ - SO_2ONa \\ - NO_2 \end{array}$$

Theory		Found	
H_2O	5.48	5.46	5.57
$4H_2O$	18.82	18.58	18.36
Na	7.39	7.33	7.40

Lead Salt.

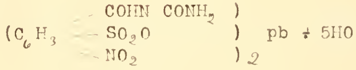
This salt was made by neutralizing a solution of the free acid with lead carbonate. It ~~was~~ is quite soluble in water separating out in thick poorly defined prisms of a pale yellow color. It crystallized with five molecules of water of crystallization, and effloresced on exposure to the air.

.1043 g. gave .0106 g. H_2O

.2115 g. gave .0216 g. H_2O

.1596 g. gave .0620 g. pb SO_4

.2394 g. gave .0932 g. pb SO_4

Calculated for 

$$\left(C_6H_3\begin{cases}COHN\ CONH_2\\ SO_2O\\ NO_2\end{cases}\right)_2 pb + 5HO$$

Theory		Found	
$5H_2O$	10.31	10.16	10.21
pb	26.38	26.50	26.56

Copper Salt.

This salt was made by dissolving freshly prepared copper oxide in a solution of the free acid. It crystallizes in small blue prisms, ~~was~~ is quite soluble in water and contains three molecules of water of crystallization.

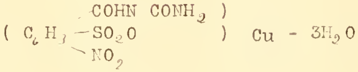
.1437 g. gave .0109 g. H_2O

.1314 g. gave .0102 g. H_2O

.2969 g. gave .0374 g. CuO.

.1691 g. gave .0170 g. CuO

Calculated for



$$\left(C_6H_3 \begin{cases} COHN\ CONH_2 \\ SO_2O \\ NO_2 \end{cases} \right) Cu - 3H_2O$$

Theory		Found	
$3H_2O$	7.78	7.59	7.76
Cu	9.91	10.03	10.06

Silver Salt.

The silver salt was prepared by dissolving silver oxide in a solution of the free acid. It crystallizes in long irregular prisms, ~~was~~ is moderately soluble in water, and contains one molecule of water of crystallization. It darkens on exposure to light.

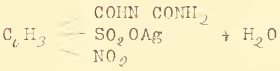
.1531 g. gave .0064 g. H_2O

.1732 g. gave .0072 g. H_2O

.1622 g. gave .0444 g. Ag

.1438 g. gave .0392 g. Ag.

Calculated for

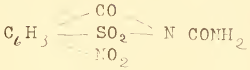


$$C_6H_3\begin{cases}COHN\ CONH_2\\ SO_2OAg\\ NO_2\end{cases} + H_2O$$

The ammonium salt of paranitrobenzoylureaorthosulphonic acid was a secondary product formed after the heated mass had been dissolved in water. The hydrochloric acid in the aqueous solution probably decomposed the original compound with the formation of ammonium chloride. All attempts to isolate the original compound failed. The mass of chloride and urea after heating was extracted with ether and chloroform, but nothing was obtained. It completely dissolved in alcohol, showing that the ammonium salt was not the original compound. It was deliquescent and very soluble in alcohol or water. No intermediate products of the reactions were ever isolated from the large amount of urea present.

There are two possible theories to account for the formation of the ammonium salt, as was the case with the ammonium salt of benzoylurea orthosulphonic acid. One mole-

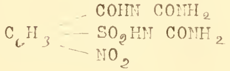
cule of urea may have reacted with one molecule of the chloride to form a ureid compound



$$C_6H_3\begin{cases}CO\\SO_2\end{cases}\!\!N\ CONH_2 \quad NO_2$$

which on hydrolysis would take up a molecule of water and give the free sulphonic acid. This with the ammonium chloride formed from the decomposition of the urea hydrochloride would give the ammonium salt.

The other explanation is that two molecules of urea may have reacted with one molecule of the chloride to form a diureid compound



$$C_6H_3\begin{cases}COHN\ CONH_2\\SO_2HN\ CONH_2\\NO_2\end{cases}$$

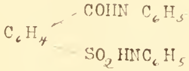
The urea residue in the sulphonyl group was then hydiolized to the ammonium salt. This view seems the most[12] probable.

Action of Aniline upon the Chlorides of Orthosulphobenzoic Acid.-

The action of aniline on these chlorides has been the subject of numerous investigations as it was from a study of these derivatives that their isomeric structure was first recognized. Three products were isolated, a sym-

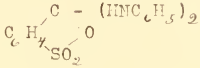
metrical anilid, an unsymmetrical anilid, and an anil. These were clearly shown to have the following structure.

Symmetrical Anilid



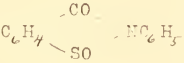
$C_6H_4 \begin{smallmatrix} COHN\ C_6H_5 \\ SO_2HNC_6H_5 \end{smallmatrix}$

Unsymmetrical Anilid



$C_6H_4 \begin{smallmatrix} C - (HNC_6H_5)_2 \\ SO_2 \end{smallmatrix} O$

Anil



$C_6H_4 \begin{smallmatrix} CO \\ SO \end{smallmatrix} NC_6H_5$

It was found that when aniline was added to an emulsion of the symmetrical chloride in a large amount of cold water, and the reaction allowed to proceed slowly, only the symmetrical anilid and the anil were formed. With the unsymmetrical chloride under similar conditions only the two anilids were obtained but with a much larger per cent of the unsymmetrical anilid. These facts form one of the chief arguments for the assignment of the symmetrical and unsymmetrical formulae to the chlorides melting at 79° and 40°.

List and Stein (1) have recently tried the reaction of aniline on these chlorides. They brought the chloride and aniline together in a cold ethereal solution and obtained from each chloride all three products. They thus claimed

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(1) B. p. 1658 1898

that the action of aniline on the chlorides afforded no good grounds for assigning the symmetrical or unsymmetrical structure to either chloride. In view of their criticism a careful study of the action of aniline on each chloride was made under various conditions.

The relative amounts of the products formed depends largely upon the method employed for bringing the aniline and chloride together. The temperature at which the reaction takes place has a large influence upon the results. Either chloride when heated with aniline alone gives a mixture of all three products, the reaction being very violent in case of the unsymmetrical chloride. When the symmetrical chloride is dissolved in anhydrous ether or chloroform and aniline added no reaction takes place. If this solution is heated on a water-bath reaction takes place only when the ether or chloroform has been expelled. This is equivalent to heating the chloride and aniline together and all three products are obtained. When the unsymmetrical chloride is dissolved in anhydrous ether or chloroform and aniline added, reaction takes place at once and all three products are obtained.

The best method is to add the aniline to an emulsion of the chloride in a large amount of cold water. Reaction

takes place slowly without the evolution of heat. With the symmetrical chloride only the symmetrical anilid and anil are obtained while with the unsymmetrical chloride both anilids are obtained but with a much larger per cent of the symmetrical anilid. The following results confirm the previous work done in this laboratory.

Aniline with the Symmetrical Chloride.

Three grams of finely powdered chloride were placed in a 250c.c. Erlenmeyer flask with about 150c.c. of water. Aniline in the proportion of four molecules of aniline to one of the chloride was then added and the contents of the flask vigorously shaken. At first there was no apparent reaction, the chloride simply going into solution with the aniline. After the lapse of three or four hours the aniline solution gradually solidified. The solid mass was then broken up and more aniline added. The resulting viscous mass was allowed to stand for two days with occasional shakings. The temperature of the water throughout the experiment averaged very nearly 14°.

Hydrochloric acid was then added. the contents of the flask transferred to a mortar and thoroughly ground up to remove the excess of aniline. The filtrate was evaporated and examined for any trace of the unsymmetrical anilid.

If present, this substance would appear in the filtrate as it is sparingly soluble in water and is not decomposed by hydrochloric acid. No trace of the unsymmetrical anilid could be obtained from the filtrates of a large number of experiments.

The residue was then treated with a dilute solution of sodium hydroxide. The undissolved precipitate consisted only of the anil ~~product~~. The filtrate yielded on acidifying with hydrochloric acid only the symmetrical anilid. From this precipitate or filtrate no trace of the unsymmetrical anilid could be obtained. The products of the reaction were only the anil and the symmetrical anilid. The chloride unaccounted for in the results was hydrolyzed to orthsulphobenzoic acid.

Chloride used	Total product.	Anil	Symmet. Anilid.
3 g.	3.19 g.	1.96 g.	1.23 g.
3 g.	3.15 g.	1.80 g.	1.35 g.
3 g.	3.20 g.	1.94 g.	1.26 g.
3 g.	3.24 g.	1.98 g.	1.26 g.
3 g.	3.36 g.	2.01 g.	1.35 g.

Chloride converted to Anil.	Chloride converted to Symmet. Anilid	Chloride unused.
1.81 g.	.84 g.	.30 g.
1.66 g.	.91 g.	.43 g.
1.79 g.	.85 g.	.36 g.
1.83 g.	.85 g.	.32 g.
1.85 g.	.91 g.	.24 g.

Aniline with the Unsymmetrical Chloride.

The same method of proce~~e~~dure was employed in these experiments, except that the flasks were kept in ice water for several hours after the experiment had started. Reaction took place much more quick~~er~~ly than with the symmetrical chloride. The aniline solution became solid in a very short time. The solid mass was then broken up and more aniline added. The viscous mass was allowed to stand for two days with occasional shakings. Hydrochloric acid was then added, the contents transferred to a mortar, and thoroughly ground up to remove the excess of aniline. From the filtrate, part of the unsymmetrical anilid was obtained. The precipitate dissolved completely in a dilute solution of sodium hydroxide showing that there was no anil formed. Hydrochloric acid precipitated a mixture of the anilids.

The precipitate was washed with a large amount of water to remove the unsymmetrical anilid. When a constant weight had been obtained the product on crystallizing from alcohol gave only the symmetrical anilid. The products of the reaction were only the symmetrical and unsymmetrical anilids, but with a much larger per cent of the unsymmetrical product. The chloride unaccounted for in the following results was probably hydrolyzed to orthosulphobenzoic acid.

Chloride used	Total prod.	Sym. Anilid	Unsym. Anilid.
3 g.	3.81 g.	1.56 g.	2.25 g.
3 g.	3.70 g.	1.42 g.	2.28 g.
3 g.	3.75 g.	1.45 g.	2.30 g.
3 g.	3.78 g.	1.49 g.	2.29 g.
3 g.	3.86 g.	1.55 g.	2.31 g.

Chloride converted to Sym.Anilid.	Chloride converted to Unsym. Anilid.	Chloride unused.
1.05 g.	1.53 g.	.42 g.
.96 g.	1.55 g.	.49 g.
.98 g.	1.56 g.	.46 g.
1.01 g.	1.56 g.	.43 g.
1.05 g.	1.58 g.	.37 g.

Erratum

I the final product in each case was

Conclusions.

Several facts have been established during this investigation.

The chlorides of orthosulphobenzoic acid can be easily obtained in any desired quantity. A new method of preparing the unsymmetrical chloride of paranitroorthosulphobenzoic acid has been devised which is much preferable to the old one.

From the action of urea on the chlorides of orthosulphobenzoic acid the final product in each case was the ammonium salt of benzoylyureaorthosulphonic acid. The intermediate products of the reaction were not isolated.

From the action of urea on the chlorides of paranitroorthosulphobenzoic acid I the ammonium salt of paranitrobenzolyureaorthosulphonic acid. The intermediate products of the reaction were not isolated.

Aniline acts upon the symmetrical chloride of orthosulphobenzoic acid with the formation of only the anil and the symmetrical anilid.

Aniline acts upon the unsymmetrical chloride of orthosulphobenzoic acid with the formation of both anilids but with a much larger per cent of the unsymmetrical product.

Biographical Sketch.

The author of this dissertation was born in Cambridge, Massachusetts, September 27, 1873. His early education was received at the public schools of that city.

In 1892 he entered Harvard University, receiving the degree of Bachelor of Arts in 1896 and Master of Arts in 1897. Since that time he has been pursuing advanced work in Chemistry at the Johns Hopkins University, taking Geology and Mineralogy as subordinate subjects.